

ANNUAL PROGRESS REPORT

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GRANT TITLE: Towards the Molecular Design of Composite Materials

REPORTING PERIOD: 1 April 1993 - 28 February 1994 (11 months)

AWARD PERIOD: 1 March 1991 - 28 February 1994

OBJECTIVE: To develop a theory of the statistical thermodynamics of polymer blends and block copolymer systems in which the theory relates microscopic and macroscopic properties and thereby assists in the molecular design of composite materials with desired macroscopic properties.

APPROACH: The lattice cluster theory for the statistical thermodynamics of polymer systems properly describes the influence of monomer molecular structure, pressure, and local correlations upon the macroscopic thermodynamic properties. The theory has been applied to study the sensitivity of various blend properties, such as the effective Flory interaction parameters, excess thermodynamic properties, phase diagrams, correlation lengths, and effective chain sizes, to monomer molecular structure and thermodynamic state. Tests of the theory are made by comparison with experimental data for selected systems and by predicting novel general trends and specific behaviors.

ACCOMPLISHMENTS: (last 11 months)

The lattice cluster theory of corrections to Flory-Huggins theory has been extended to describe the variation of the effective interaction parameter for diblock copolymers on composition, monomer molecular structure, microscopic interaction energies, and temperature. While the previous theoretical extensions have been applied to diblock copolymer melts, further lattice cluster theory computations have completed the task of computing the free energy for a ternary compressible system of diblock copolymers with their respective homopolymers. The theory is being used to study the stabilization of blends by block copolymers. Detailed computations have been performed for ternary systems with polystyrene-b-poly(methyl methacrylate), polystyrene-b-poly(vinyl methyl ether), and polystyrene(H)-b-polystyrene(D) diblock copolymers along with their respective homopolymers. The computations consider the limits of stability for the homogeneous phase as a function of the composition and molecular weights of the ternary system, demonstrating conditions under which the blend may be either stabilized or destabilized and exhibiting substantial differences from small molecule behavior for the influence of dilution on critical properties of binary mixtures. There are likewise substantially different behaviors for blends which display lower versus upper critical solution temperatures. The lattice cluster theory has also been used to study the molecular characteristics governing the domain in which mean field theories are

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not valid. Monomer molecular structure, equation of state effects, and local correlations are shown to exert a strong influence on the size of the non-classical region, and large departures are evidenced from the classic incompressible Flory-Huggins theory.

SIGNIFICANCE:

The stabilization of blends by block copolymers is an important phenomenon in controlling the properties and morphology of polyolefins which are of importance as structural materials such as high impact polystyrene which is a two-phase blend of polystyrene and polybutadiene as well as block copolymers of these species. Our computations demonstrate that a much richer variation of the phase behavior (and hence of the physical properties) is predicted to arise from the combined influences of local correlations, monomer molecular structure, and equation of state effects. Such rich variation provides more opportunities for the design and control of new structural materials with improved adhesive characteristics. A theory for the size of the non-classical region in binary polymer blends is essential in interpreting experiments on the dynamics of phase separations in these systems. Very different theories apply in the classical, non-classical, and cross-over domains. Our theory exhibits gross departures from the predictions of the classic, but over simplistic Flory-Huggins theory, and we explain the origins for the observed lack of universality of the previously derived expressions for the size of the non-classical domain.

WORK PLAN (NEXT 12 MONTHS):

The URI grants are non-renewable, and other sources of funding will be sought for a continuation of this work. Several promising directions exist for extending and applying our lattice cluster theory. We believe that our advances with the lattice cluster theory will also find important applications to biophysical problems as evidenced by the interest of persons like Dill in our theoretical methods.

PUBLICATIONS AND ABSTRACTS:

1. Lifschitz, M., Dudowicz, J. and Freed, K.F. (1994) Limits of Validity for Mean Field Description of Compressible Binary Polymer Blends. J. Chem. Phys. 100: 3957.
2. Dudowicz, J. and Freed, K.F. (1994) Towards a Molecular Theory of Polymer Blends. Makromol. Chem., Macromol. Symp. 78: 39.
3. Dudowicz, J. and Freed, K.F., Lattice cluster theory for the stabilization of blends by block copolymers. Manuscript in preparation.
4. Freed, K.F. (1994) Towards a molecular theory for the properties of polymer blends. Polym. Preprints.

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TOWARDS THE MOLECULAR DESIGN OF COMPOSITE MATERIALS

LATTICE CLUSTER THEORY FOR POLYMER BLENDS

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Objectives

- Develop theory of statistical thermodynamics of polymer systems with following features:
 - Describes influence on monomer structure
 - and on thermodynamic state
 - Includes influence of local correlations
 - Relates macroscopic and microscopic properties in predictive fashion
 - Explain dependences of phase behavior and physical properties on architectures, e.g., blends vs. block copolymers

Accomplishments

- Extend lattice cluster theory to describe phase behavior for systems of diblock copolymers and their homopolymers
- Predict stabilization or destabilization of blends by block copolymers depending on block composition, molecular weights, and whether blend has lower or upper critical solution temperatures
- Explain observed nonuniversality for measures of the non-classical domain in blends and give predictions of rich possible behavior

Significance

- Ternary blend-homopolymers important as structural materials, emulsions, etc.
- Theory predicts wide range of possible phase behavior, leading to more ways to control morphology and properties of system.
- Theory of non-classical region important for guiding experiments on the dynamics of phase separation for varying depths of temperature quenches and for the complete range of blend compositions, molecular weights, and pressures